

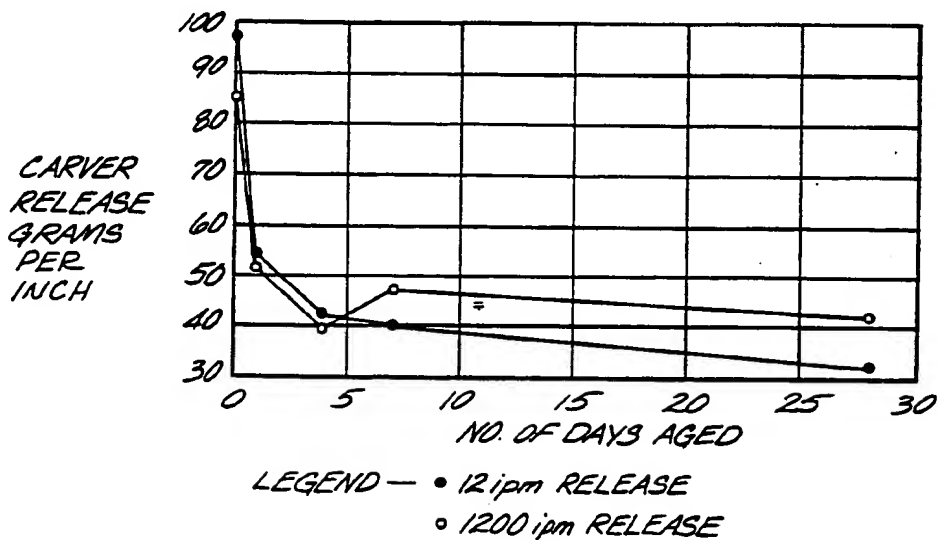


INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 4 : B32B 9/04		A1	(11) International Publication Number: WO 88/ 07931
			(43) International Publication Date: 20 October 1988 (20.10.88)
(21) International Application Number: PCT/US88/01160		(74) Agents: GRINNELL, John, P. et al.; Christie, Parker & Hale, Post Office Box 7068, Pasadena, CA 91109-7068 (US).	
(22) International Filing Date: 1 April 1988 (01.04.88)			
(31) Priority Application Number: 036,253		(81) Designated States: AT (European patent), AU, BE (European patent), BR, CH (European patent), DE (European patent), FI, FR (European patent), GB (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent).	
(32) Priority Date: 9 April 1987 (09.04.87)			
(33) Priority Country: US			
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(54) Title: IMPROVED RELEASE COATINGS

RT AGING



(57) Abstract

Excellent release surfaces are formed by curing a composition which is a dispersion of a reactive silicone present in an amount of from 1 to 30% by weight of the composition as a discontinuous phase in a continuous phase of a reactive resin comprising a reactive oligomer and optionally a reactive monomer. The product has a silicone release surface with silicone anchored in the coating. The surface is for releasable contact with a pressure-sensitive adhesive. Heat, electron beam and/or ultraviolet radiation may be used to achieve cure.

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IMPROVED RELEASE COATINGS

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Background of the Invention

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The construction of pressure sensitive adhesive products presents a variety of materials selection problems. Basic to any construction is the selection of a suitable release surface.

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A label, for instance, is normally comprised of a face stock which may range from paper to a plastic film such as polyester film or even metal; a release liner having a silicone release surface, and a pressure-sensitive adhesive layer, normally rubber or acrylic based in contact with the face stock and the silicone release surface. In self-wound products, a silicone release may be applied to the face stock opposite the side to which the adhesive is applied.

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Conventional silicone release coatings are essentially 100% by weight as a silicone resin on a solids basis and by weight the most expensive raw material in label and tape constructions. It would be desirable to reduce the amount of silicone employed as this would reduce the cost of the silicone release surface. Reducing silicone content, however, has a normal effect of increasing the bond to the release surface. As dilution occurs a point is reached where the bond becomes so great that the adhesive may sever the silicone material from the substrate, normally paper, to which it was applied and

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1 in effect transfer the silicone to the adhesive to the
detriment of the ability to bond the adhesive to another
surface.

5 U.S. Patent 4,288,479 to Brack is directed to release
coatings which contain a waxy material of limited com-
patibility with a liquid monomer or prepolymer. Upon
application to a film, the waxy material migrates to the
surface. Radiation is applied to cure the polymer. The
10 waxy material which include silicones are described as
generally non-reactive in the polymerizable liquid but
can contain reactive groups. In Example 65 of the Brack
patent, there is described a release composition containing
a silicone rubber which was a polydimethyl siloxane with
some unsaturation. On radiation there was stated to be
15 formed a surface releasable with respect to a removable
adhesive. We have found that the composition is not
functional for permanent pressure sensitives which differ
from removable adhesives in that adhesive bond grows
with time. As established here, the combination welded
20 together. See Example 5 herein.

The present invention is directed to novel
formulations of substantially reduced silicone content
which display excellent release properties.

25 Summary of the Invention

There is provided a substrate having bonded thereto
a cured release coating having a silicone release surface
for contact with a pressure-sensitive adhesive formed by
coreaction of components of a coating composition of a
30 silicone comprised of dimethyl siloxane polymers, prefer-
ably a reactive silicone and a resin preferably a reactive
resin. The silicone is present in an amount of from
about 1 to about 30 percent by weight of the coating
composition and anchored to the coating so as to be
35 substantially non-transferable to a pressure-sensitive

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1 adhesive. The silicone release surface is functional to
release permanent and removable pressure-sensitive adhe-
sive.

5 Cure is preferably induced by the action of heat,
actinic radiation and/or electron beam radiation, provided
in a quantity sufficient to anchor the silicone to the
resin whereby the silicone becomes substantially non-
transferable to a pressure-sensitive adhesive. Ultraviolet
and/or electron beam radiation is presently preferred.

10 The silicones employed preferably have a molecular
weight of at least about 2,000, preferably 10,000 or more.

It is presently preferred that the products be
formed by curing a coating comprised of from about 1 to
about 30 percent by weight, preferably from about 5 to
15 about 30, most preferably from about 5 to about 15 percent
by weight, of a reactive silicone dispersed as a discon-
tinuous phase in a reactive resin present in an amount
of from about 99 to about 70 percent by weight, preferably
from about 95 to about 70 percent by weight, more prefer-
20 ably from about 95 to about 85 percent by weight, of the
combination of the reactive silicone and reactive resin.
The reactive resin contains from about 50 to 100 percent
by weight reactive oligomer and from about 50 to 0 percent
by weight reactive monomer based as the total weight of
25 reactive oligomer and reactive monomer. The reactive
monomer is used to control viscosity prior to cure.

To enable good coatability, the dispersion preferably
has a viscosity of from about 300 to about 10,000 cps.
There may also be included in the system as required photo-
30 initiators, colorants and the like.

The invention enables tailoring of the silicone
release surface to the product. Useful products will
have TLMI (Tape and Label Manufacturers Institute) peel
under Keil conditions of no greater than about 400 N/M.
35 For tapes the TLMI peel should be no greater than about

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1 400 N/M, more typically 100 to 200 N/M. For tags and
labels a "high release specification has a TLMI peel up
to about 60 to about 100 N/M; a "medium" release has a
5 TLMI peel of about 20 to about 50 N/M; and a "low release"
has a TLMI peel of less than about 20. Again all peel
values are reported for Keil conditions, namely after
aging at a load of 0.25 psi for 20 hours at 70°C.

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1 Brief Description of the Drawings

FIG. 1 illustrates Carver release in grams per inch as a function of aging at room temperature for the composition described in Example 1.

5 FIG. 2, the Carver release is for the same composition except for aging at 140°F.

FIG. 3 illustrates the release as a function of silicone content of the coating at the time of cure.

10 FIG. 4 illustrates the same release but after aging for 28 days at room temperature.

FIG. 5 is for the same composition but after aging 28 days at 140°F.

FIG. 6 shows the effect of concentrations of photo initiator on the release force and its effect with time.

15 Attached drawing marked "Prior Art" depicts the accepted effect on a control release additive on a silicone release material. As can be appreciated by inspection, the release force remains fairly constant until some point is reached where the force increases dramatically. On
20 the scale, zero designates no control release additive while 1 designates no silicone polymer.

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1 Detailed Description

 There is provided in accordance with the present invention a substrate having thereon a cured coating of silicone release surface for contact with a pressure-sensitive adhesive. The coating is formed by coreaction of a silicone comprised of dimethyl siloxane polymers, preferably a reactive silicone and a resin, preferably a reactive resin comprising a reactive oligomer. Under curing conditions induced by application of sufficient heat, electron beam (EB) radiation and/or actinic radiation, preferably ultraviolet (UV) radiation, the silicone is anchored to the cured coating and is rendered substantially non-transferable to a pressure-sensitive adhesive in contact with the release surface. The dimethyl siloxane polymer content of the coating is from about 1 to about 30 percent by weight on the total weight of the constituents of the coating with the anchored silicone preferentially concentrated at the surface provided for contact with a pressure-sensitive adhesive. The cured coating may be achieved using silicone-monomer combinations.

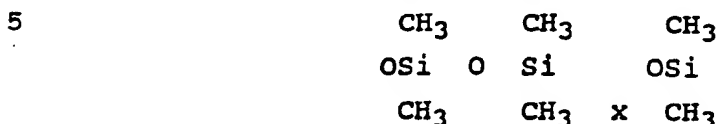
 Preferential presence of silicone at the surface may be achieved by partial to total incompatibility of the silicone and the resin, or by structural rearrangement of a silicone-resin surface. What is critical is that the silicone is sufficiently anchored to the surface and substantially non-transferable to a pressure-sensitive adhesive. Anchoring may be mechanical and/or chemical.

 The desired products have a Carver release as defined herein of less than about 100 grams per inch. Carver release is determined by applying ScotchTM 610 tape to the release surface under a pressure of 6000 psi for 60 seconds then measuring force required to achieve release at a peel rate of 12 inches per minute.

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1 As used herein, by the term "silicone" there is meant dimethyl siloxane polymers consisting of alternate silicone and oxygen atoms with methyl groups attached to silicone. The general structure is:



wherein "x" is an integer.

10 By the term "reactive silicone" there is meant a silicone end capped and/or mid-chain substituted with groups reactive on application of heat and/or energy with reactive groups of the resin. The presently preferred reactive groups are acrylic, mercapto and/or oxirane.

15 By the term "resin" there is meant an organic moiety which is combinable with the silicone and reactive with silicone and/or reactive silicone under action of heat, actinic radiation and/or electron beam radiation to cause anchoring, preferably preferential surface anchoring of the silicone to the resin.

20 By the term "reactive resin" there is meant a resin comprising reactive oligomers containing groups which are reactive with the reactive groups of a reactive silicone. The presently preferred reactive oligomers contain reactive acrylic, mercapto and/or oxirane groups.
25 The reactive resin may include a reactive monomer used to control viscosity, although not necessary to utility of the silicones.

30 By the term "reactive monomer" there is meant monomers which coreact with the reactive silicone and/or the reactive oligomer of the reactive resin and which are effective in reducing viscosity of coating composition used to form the end products of this invention. It is preferred that the reactive monomer be a multifunctional monomer preferably a multifunctional acrylate.

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1 By the term "silicone release surface" there is
meant a surface which will release from a pressure sen-
sitive adhesive substantially without transfer of release
material to the adhesive and having a TLMI peel under
5 Keil conditions of no greater than about 400 N/M.

It is presently preferred that the products of the
invention be formed by coating a substrate such as paper
then curing the coating, where the coating is comprised
of from about 1 to about 30 percent by weight, preferably
10 about 5 to about 30 percent by weight, more preferably
about 5 to about 15 percent by weight, of a reactive
silicone dispersed as a discontinuous phase in a reactive
resin present in an amount of from about 99 to about 70
percent by weight, preferably from about 95 to about 70
15 percent by weight, more preferably from about 95 to
about 85 percent by weight of the combination of the
reactive silicone and reactive resin. The reactive
resin contains from about 50 to 100 percent by weight
reactive oligomer and from about 50 to 0 percent by
20 weight reactive monomer based as the total weight of
reactive oligomer and reactive monomer. The reactive
monomer is used to control viscosity prior to cure.
There may also be included in the system as required
photoinitiators, colorants and the like.

25 To enable good coatability, the dispersion should
have a viscosity of from 300 to about 10,000 cps. Vis-
cosity can, as indicated, be adjusted by the addition of
reactive monomers.

While not bound by theory, it is presently believed
30 that surface reorientation occurs to form the silicone
release surface. Reorientation can occur either prior to,
during or following cure, as it has been observed, the
quality of release of the silicone release surface can
increase with time, even a fairly short time span, and
35 then level out. Improved release is attributed to the

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1 amount of silicone at the surface. The cured coating is
believed similar to block or graft copolymers having
oligomer blocks bound to the silicone blocks with pref-
5 erential presence of silicone at the surface as opposed
to the body of the coating. The coating typically has a
glass transition temperature of at least 0°C, preferably
greater than about 20°C.

Critical to the use of a dispersion is that the
proportion of reactive silicone and reactive resin remain
10 as a coatable dispersion in which the reactive silicone
is as the dispersed phase and the reactive resin is the
continuous phase. Once a certain level of reactive
silicone monomer content is reached, phase inversion
begins, to the end of forming a system in which the
15 reactive resin is the dispersed phase and the reactive
silicone is the continuous phase. When this is complete,
the cured product will become rubbery and behave like a
conventional silicone release coating which requires a
high concentration of silicone before a suitable release
20 level is achieved.

In the practice of the invention, the dispersion is
coated in a conventional manner onto a substrate which may
be any grade of paper, including the papers of low grade,
cardboard, polymeric films and the like. Cure is to be
25 sufficiently complete, such that substantially no silicone
transfers to a pressure-sensitive adhesive to which the
silicone release surface contacts. Avoidance of transfer
is the result of the silicone being anchored to coating
body and not available to transfer to the pressure-sen-
30 sitive adhesive.

Electron beam cure has a particular benefit, since
it can initiate reaction of resins with substantially
non-reactive silicones to produce a functional release
surface. The ability of the coating to accept colorants

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1 is a desirable feature for establishing the presence and
uniformity of the release coating.

What is produced by the practice of the invention
is a unique product of low silicone content but having a
5 silicone release surface having excellent release prop-
erties. The coating is hard and substantially non-stretch-
able and aggressively bound to the substrate to which it
is applied. Substantially complete cure insures against
transfer to the adhesive during the lifetime of a laminate
10 or self-wound product. The release coatings of this
invention provides the advantage that the release force
can be relatively constant over broad range of stripping
speeds without the silicone substantially transferring
to the adhesive surface. High holdout can be achieved
15 on low grade papers and monomers can be used not only to
adjust viscosity but also adjust release force.

In the following Examples TLMI Release is by Test
Method VII LD-468 and PSTC Test No. 2. Loop Tack is by
PSTC - Test No. 5. Keil release values are after aging
20 under a force of 0.25 psi for 20 hours at 70°C. TLMI means
Tape and Label Manufacturers Institute and PSTC means
Pressure Sensitive Tape Council. Except for the removable
adhesive identified as part of Example 1, the adhesives
employed in the Examples were permanent rubber based
25 and/or acrylic based pressure-sensitive adhesives.

EXAMPLE 1 (FIGS. 1-6)

A master batch of a resin coating designated as AE-
508 was formed of 72 parts by weight acrylated epoxy
30 oligomer (Celanese 3703) supplied by Celanese Corp., 16
parts by weight hexanedioldiacrylate (HDODA) and 12
parts by weight diethoxyacetophenone (DEAP). From 80-95
parts of the master batch was mixed with 20-5 parts
DehesiveTM VP-1530, a mixture acrylated and thiol and func-
35 tional polysiloxanes, available from Stauffer-Wacker

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1 Silicones Co. (S-1530 herein). The mixtures were prepared
in select increments of weight percent silicone.

The coating mixtures were applied on clay coated
gloss paper.

5 The coated paper was exposed to the UV radiation
given off by two medium pressure mercury vapor lamps at
200 watts/inch at web speed of 50 feet per minute. This
corresponds to an energy input of about 5 kilojoules per
square meter. Exposure resulted in cure to a hard glossy
10 film which was dry to the touch. Completeness of cure
was determined by laminating ScotchTM 610 tape manufac-
tured by 3M, under pressure and measuring the force
required to delaminate the construction or remove the
tape. Release which is stable and low over time without
15 substantially detackifying the adhesive is one indication
of complete cure.

Cured coatings with varying amounts of S-1530 were
tested using the Carver release test which consists of
laminating the cured release liner to ScotchTM 610 tape
20 under a pressure of 6,000 psi for 60 seconds, and measuring
force required to achieve release at a peel rate of 12
inches per minute (ipm). Release measurements were
modified to include a 1200 inches per minute (ipm) rate.
The release test as applied to aged samples was after
25 aging with the test tape applied just before measuring
release values.

The initial formulation consisted of 90% AE 508 and
10% S-1530. As shown in FIGS. 1 and 2, the initial
Carver Release values were between 80-100 grams. Aging
30 at room temperature or 140°F, resulted in a rapid decline
to a stable release level within the range of 20-50 grams.

FIGS. 3, 4 and 5 show the results of varying the
concentration of S-1530 on Initial Peel (FIG. 3) after
room temperature (RT) aging (FIG. 4) and elevated tempera-
35 ture aging (FIG. 5). The results display a phenomenon

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1 that appears to be related to phase transition. As
silicone content increases there is reached a point where
a transition to a rubbery phase occurs. The system then
behaves in a conventional way, with release force de-
5 creasing with an increase in silicone content.

More particularly, FIG. 3 shows the initial Carver
Release results and shows low initial releases (both 12
and 1200 ipm) in the range of 3%-5% S-1530. In the range
of 10%-40% S-1530 initial release values increase, with
10 1200 ipm releases actually appearing to be lower than 12
ipm. By 40%, S-1530 12 ipm release values decline while
1200 ipm releases increase rapidly and appear to level
off above 50% S-1530.

FIGS. 4 and 5 show the Carver release values for
15 samples aged 28 days at RT and 140°F. Formulations in
the 5%-20% S-1530 range yield release values in the range
of 20-40 grams with minimal differences between 12 and
1200 ipm releases. Above about 30% S-1530, the release
values climb rapidly, peak, and then decline as the
20 percentage of S-1530 increases beyond 40%. The range
beyond 60% S-1530 is again characterized by a marked
difference between 12 and 1200 ipm release values. The
region up to 20 percent is hard and glassy with desirable
release values. Above about 30% S-1530 a phase inversion
25 occurs to a rubbery phase which is characteristic of
conventional release liners.

The concentration of photoinitiator diethyl aceto-
phenone (DEAP) in the formulation has a significant
effect on the initial Carver release values of lab samples.
30 As shown in FIG. 6, the formulation with an excessive
amount of DEAP (20%) yields initially high Carver release
values, which subsequently age down to a level similar
to formulations with 1%-5% DEAP. This is similar to the
aging down observed in FIGS. 1 and 2 are for formulations
35 having a concentration of 10.8% DEAP.

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1 Constructions using a rubber based hot melt removable
adhesive and a high tack, high peel rubber based hot
melt adhesive, were made and found to have acceptable
low release from the surface to 10% S-1530. Constructions
5 using 4, 6 and 10% S-1530 were prepared using a removable
adhesive. Formulations using 6 and 10% S-1530 had low
release whereas the formulation using 4% silicone had
tighter release as measured by subjective testing.

10

EXAMPLE 2

 There was evaluated the performance of AE-508 with
various reactive silicones as against their performance
as homopolymers. The control was a standard thermally
cured silicone release liner. The reactive silicones
15 were S-450, an end acrylated silicone known as RC-450
supplied by Goldsmith Chemical Corporation; S-1559, a
mixture of acrylated and mercapto functional silicone
known as DehesiveTM VP-1559 supplied by Stauffer Wacker-
Silicone Corp.; S-4818, an end and in chain acrylated
20 silicone known as IC-4818-38 supplied by Lord Chemical
Company and S-5360 and S-6350, each end and in chain
acrylated silicones known respectively as Ebecryl 19-
6360 and 19-6350, supplied by U.C.B. Radcure Inc.

 Table 1 shows performance with an acrylic adhesive
25 while Table 2 shows performance with a rubber based
adhesive. In the Table, homopolymer means 100% of the
reactive silicone; copolymer means 80% by weight AE-508
and 20% by weight reactive silicone. In each instance
the coating was formed on a super calendered kraft paper
30 and EB cured at a dosage of 30 kGy.

 The conclusion drawn was that the copolymers served
as useful release agents as did the most costly homo-
polymers.

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TABLE 1

	<u>Homopolymer</u>	<u>TIM1 Peel</u> <u>300 ipm(N/M)</u>		<u>Loop Tack (N/M)</u>
		<u>3 Day</u>	<u>Keil</u>	<u>3 Day</u>
5	S-450	69	54	450
	S-1559	22	44	340
	S-4818	18	40	405
	S-6360	134 ¹	138 ¹	335
	S-6350	119	168	130
	<u>Copolymer</u>			
10	S-450	64 ¹	36 ²	165
	S-1559	36	28 ²	455
	S-4818	30 ^{1,2}	37 ²	445
	S-6360	60 ^{1,2}	46 ^{1,2}	515
	S-6350	87 ^{1,2}	111 ²	515
	<u>Control</u>	6	6	400

1 Release Pickoff at Slow Speeds
2 Zippy Release

TABLE 2

	<u>Homopolymer</u>	<u>TIM1 Peel</u> <u>300 ipm(N/M)</u>		<u>Loop Tack (N/M)</u>	
		<u>3 Day</u>	<u>Keil</u>	<u>3 Day</u>	<u>Keil</u>
20	S-450	4	7	1895	1980
	S-1559	5	8	1615	1655
	S-4818	3	5	1575	1715
	S-6360	5	22 ²	1720	1850
25	S-6350	8	12 ²	1065	1280
	<u>Copolymer</u>				
	S-450	7	10	1870	1835
	S-1559	6	5	1790	1655
	S-4818	4	4	1770	1495
30	S-6360	26 ²	39 ¹	1990	1750
	S-6350	14 ²	20 ²	1950	1695
	<u>Control</u>	4	6	1625	1590

1 Release Pickoff at Slow Speeds
2 Zippy Release

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EXAMPLE 3

The following is to show the effect of using the
 different oligomer and monomer combinations to enable
 control of release. With reference to Table 2, resins
 19-6810, 19-6830 and 19-6657 are acrylated polyesters
 sold by U.C.B. Radcure, Inc.; PES-166 and PES-169 are
 acrylated urethanes sold by Polymer Systems Corporation;
 "BPA diacryl" is an acrylated bisphenol-A epoxy resin;
 C-9003 is an aliphatic triacrylate. The control was a
 commercial release liner having a 100% silicone surface.
 The adhesive employed was a tackified Kraton-1107, a
 styrene-isoprene, styrene-isoprene-styrene resin rubber
 manufactured and sold by Shell Chemical Company. The
 formulation in each instance was 70% by weight resin or
 monomers, 20% by weight hexanedioldiacrylate (HDODA) and
 10% by weight S-1559. Cure was by electron beam at a
 dosage of 30 kGy in the presence of 200-250 ppm oxygen.
 Results shown in Table 3 established that epoxy, urethane
 and polyester oligomers gave low release values whereas
 an aliphatic oligomer gave higher release.

TABLE 3

	<u>Resin</u>	<u>Description</u>	<u>TIME RELEASE (N/M)</u>		<u>LOOP TACK (N/M)</u>	
			<u>One Day</u>	<u>Keil</u>	<u>One Day</u>	<u>Keil</u>
25	19-6810	Polyester	7	14	590	630
	19-6830	Polyester	34	26	980	690
	19-6657	Polyester	19	22	690	710
	PES-166	Urethane	1	10	690	710
	PES-169	Urethane	8	11	670	650
30	SR-349	BPA Diacryl	1	19	690	590
	C-9003	Aliphatic Triac	75	88	590	530
	Control		--	--	850	650

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EXAMPLE 4

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In Example 65 of U.S. Patent 4,228,479 to Brack, there is disclosed a potential formulation for a release surface. The formulation was prepared with certain substitutions made because of the lack of availability of components. The substitutions were not believed to modify the performance as the controlling ingredient was the silicone employed. The base formulations are shown in Table 4.

10

TABLE 4COMPONENTSEXAMPLE 65FORMULATION A

66 Parts	Trifunctional Urethane	PES-166 Difunctional Urethane
68 Parts	1,4-Butane Diol Diacrylate	1,6 Hexane Diol Diacrylate
15 50 Parts	Acrylated Epoxidized Soya Oil	same
72 Parts	Trimethylolprop. Tri Acry	same
1.5 Parts	2-Hydroxy Ethyl Acrylate	1,4-Butane Diol Monoacrylate
2 Parts	Stearyl Acrylate	same
5 Parts	W-982 Silicone Gum (0.2% vinyl)	Several Variations
16 Parts	Benzoin Isobutyl Ether	Benzoin Isopropyl Ether

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Since Brack taught the use of a silicone of low functionality there was employed as a representative of the silicone contemplated by the patentee, 0.2% VOC, which was a 0.2% vinyl end capped polydimethyl siloxane. Their performance with respect to a hot melt rubber base adhesive and an acrylic adhesive are formulations A to B of Tables 5 and 6. UV cured formulations as suggested by Brack were regarded as nonfunctional as a release surface as the Keil values for the loop tack could not even be measured due to welding. It was surprisingly found that high energy dosage available by electron beam cure could produce functional release materials. When formulation A was used with the silicones of the instant invention, namely formulations C and D, they as well as formulations E to H at all times a functional release surface formed under both UV and EB conditions. In the process,

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1 a master batch of all components except the silicone
 formulation was prepared. The various formulations were
 prepared by taking a portion of the master batch and
 adding the silicone and photo-initiators as required.
 5 Samples were coated on super-calendared kraft paper and
 cured by either UV or EB radiation. The cured samples
 were then laminated to freshly prepared dry adhesives on
 polyester films. They were aged for one day under Keil
 conditions (70°C, 0.25 psi for 20 hours) and TlMI release
 10 measured at 300 inches per minute; the results including
 loop tack data measured are reported in Tables 5 (rubber
 based permanent adhesive) and 6 (acrylic based permanent
 adhesive).

TABLE 5

15

	<u>Form</u>	<u>Resin</u>	<u>Silicone</u>	<u>SI%</u>	<u>Cure</u>	<u>TlMI Release(N/M)</u>		<u>Loop Tack(N/M)</u>	
						<u>One Day</u>	<u>Keil</u>	<u>One Day</u>	<u>Keil</u>
	A	A	0.2% VEC+BIPE	1.8	UV	40	WELD	1340	--
	B	A	0.2% VEC+BIPE	10	UV	35	WELD	700	--
20	C	A	S-1559	1.8	EB	7	32	1880	1830
	D	A	S-1559	10	EB	7	24	1450	1720
	E	AE-508	S-1559+BIPE	10	UV	2	1	1000	900
	F	AE-508	S-1559+12BIPE	10	UV	2	1	1240	920
	G	AE-508	S-1559+12DEAP	10	UV	35	5	1140	1150
	H	AE-508	S-1559	10	EB	6	12	1635	1700
		Control		100	--	3	8	1700	1750

25

Form = Formulation

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TABLE 6

	<u>Form Resin Silicone</u>			<u>SI%</u>	<u>Cure</u>	<u>TIME Release(N/M)</u>		<u>Loop Tack(N/M)</u>	
						<u>One Day</u>	<u>Keil</u>	<u>One Day</u>	<u>Keil</u>
5	A	A	0.2% VEC+BIPE	1.8	UV	140	WELD	—	—
	B	A	0.2% VEC+BIPE	10	UV	160	WELD	—	—
	C	A	S-1559	1.8	EB	110	93	420	520
	D	A	S-1559	10	EB	100	30	370	340
	E	AE-508	S-1559+BIPE	10	UV	30	55	300	220
	F	AE-508	S-1559+12BIPE	10	UV	25	50	—	300
	G	AE-508	S-1559+12DEAP	10	UV	55	67	—	160
	H	AE-508	S-1559	10	EB	70	100	420	550
10	Control			100	—	100	150	400	220

Cure Dose: EB=30KGy;UV=2x200Watts/Inch Lamps, 50 ft/min.

VP-1559 Radiation Curable Silicone Coating from SWS Silicones

0.2% VEC = 0.2% Vinyl Encapped Polydimethylsiloxane

BIPE=6% Benzoin Isopropyl Ether, 12BIPE=12% Benzoin Isopropyl Ether

12DEAP=12% Diethoxyacetophenone

15 Form = Formulation

EXAMPLE 5

Formulation AE-508 was as a base formulation employing GE 479-1866 an experimental epoxy functional silicone provided by General Electric Company, Silicone Products Division. The formulations are shown in Table 7 and Carver release results reported after UV cure using 2 lamps at 200 watts per inch at a web speed of 50 feet per minute are shown in Table 8. Results are high average or highest value.

25

TABLE 7

	<u>Formulation, Percent By Weight</u>			<u>A</u>	<u>B</u>	<u>C</u>
30	AE-508			95	94	89
	GE 479-1866			5	5	10
	Additional Photoinitiator			0	1	1

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TABLE 8

<u>Carver Peel in grams/inch at</u>		<u>Formulation</u>		
		<u>A</u>	<u>B</u>	<u>C</u>
5	I. 12 ipm at			
	R.T., initial	55	7	(a)
	7 days	13	10	3
	14 days	11	-	-
	28 days	7	4	3
10	140°F - 7 days	13	12	8
	14 days	24	20	4
	28 days	13	7	4
	II. 1200 ipm at			
	R.T., initial	195	65	62
15	7 days	48	54	68
	14 days	54	60	77
	28 days	54	61	64
	140°F - 7 days	45	48	53
	14 days	57	60	71
	28 days	48	52	42

(a) Too low to measure

EXAMPLE 6

20

Tests were conducted to show the effect of using the different oligomers and silicone combinations to enable control of release. With reference to Table 9, resin ValsparTM S-9783-002 a mixture of acrylated oligomers provided by Valspar Co. was mixed with S-450 in varying amounts coated and EB cured (30kGy) on a polypropylene release backing. Peel was measured with respect to a permanent rubber based pressure sensitive adhesive.

25

TABLE 9

30			<u>KEIL</u>	
	<u>% S-450</u>	<u>% OLIGOMER</u>	<u>RELEASE (N/M)</u>	<u>180° PEEL (N/M)</u>
	5	95	300	460
	10	90	170	440
	15	85	120	440

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-20-

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EXAMPLE 7

The data of Table 10 shows the effect of using the different monomer combinations on release. The monomers were pentaerythritoltriacylate (PETA), hexanediol-
5 diacylate (HDODA) and 2-ethylhexyl acrylate (2EHA).

TABLE 10

	<u>% S-450</u>	<u>% 2-EHA</u>	<u>% PETA</u>	<u>% HDODA</u>	<u>KEEL RELEASE (N/M)</u>	<u>LOOP TACK (N/M)</u>
10	25	-	-	75	80	600
	25	25	25	25	9	650
	25	-	25	50	170	400

EXAMPLE 8

15

A mixture of 20 parts trimethylpropanetriacylate, 40 parts Celrad 3201, an acrylated polyester from Celanese, Inc., 10 parts N-vinylpyrrolidone and 1.5 parts S-6350 and-2 parts photo initiator was coated onto crepe paper and cured with enough actinic (UV) radiation to give a hard
20 dry film. The release liner was Keil aged against a permanent rubber based pressure sensitive adhesive. The Keil release forces were 80-150 N/M with minimal loss of adhesive tack.

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1 WHAT IS CLAIMED IS:

1. A product comprising a substrate having bonded thereto a cured release coating having a silicone release surface for releasable contact with a pressure-sensitive adhesive said coating formed by coreaction of a silicone comprised of dimethyl siloxane polymers and a resin contained in a coating composition applied to the substrate, the silicone being present in an amount of from about 1 to about 30 percent by weight of the coating and sufficiently anchored to the coating to be substantially non-transferable to a pressure-sensitive adhesive.

2. A product as claimed in claim 1 in which the silicone is present in an amount of from 5 to about 15 percent by weight of the coating.

3. A product comprising substrate having bonded thereto a cured release coating having a silicone release surface for releasable contact with a pressure-sensitive adhesive said coating formed by coreaction of silicone present in an amount of from about 1 to about 30 percent by weight of the coating and a resin contained in a coating composition applied to the substrate, the cure induced by exposure of the applied coating to the action of energy supplied by heat, actinic radiation, electron beam radiation, or combinations thereof induced in a sufficient amount to anchor the silicone to the coating whereby the silicone is substantially non-transferable to a pressure-sensitive adhesive.

30

4. A product as claimed in claim 3 in which the silicone is present in an amount of from about 5 to about 15 percent by weight of the coating.

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1 5. A product comprising a substrate having bonded
thereto a cured release coating having a silicone release
surface for releasable contact with a pressure-sensitive
5 adhesive and said coating formed by coreaction of a
reactive silicone present in an amount of from about 1
to about 30 percent by weight of the coating and a reactive
resin comprised of reactive oligomers contained in a
coating composition applied to the substrate, the cure
induced by the action of energy supplied by heat, actinic
10 radiation, electron beam radiation, or a combination
thereof and induced in an amount sufficient to anchor
the silicone to the coating whereby the silicone is
substantially non-transferable to a pressure-sensitive
adhesive.

15

6. A product as claimed in claim 5 in which the
silicone is present in an amount of from about 5 to
about 15 percent by weight of the coating.

20

7. A product comprising a substrate having bonded
thereto a cured release coating having a silicone release
surface for releasable contact with a pressure-sensitive
adhesive and said coating formed by coreaction of a
reactive silicone present in an amount of from about 1
25 to about 30 percent by weight of the coating and a resin
comprised of reactive oligomers, said reactive silicone
being at least partially immiscible in said coating
composition, the cure induced by the action of energy
supplied by heat, actinic radiation, electron beam radia-
30 tion, or a combination thereof induced to the coated
substrate in sufficient amount to anchor the silicone to
the coating whereby the silicone is substantially non-
transferable to a pressure-sensitive adhesive.

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1 8. A product as claimed in claim 7 in which the
silicone is present in an amount of from about 5 to
about 15 percent by weight of the coating.

5 9. A product as claimed in claim 1 which includes
a colorant.

10 10. A product as claimed in claim 7 which includes
a colorant.

15 11. A product comprising a substrate having coating
on at least one side thereof with a cured coating composi-
tion comprised of from about 1 to about 30 percent by
weight of the coating composition of a reactive silicone
dispersed as a discontinuous phase in about 99 to about
20 70 percent by weight of the coating composition or con-
tinuous reactive resin phase comprising from about 50 to
100 percent by weight of the oligomer reactive with said
reactive silicone and from about 50 to 0 percent by
25 weight of the reactive resin of a reactive monomer, said
reactive silicone being a polydimethyl siloxane having a
molecular weight of at least about 2000 and having pendent
therefrom sufficient reactive groups to react with the
reactive groups of the oligomer, said coating being cured
30 on exposure to the action of electron beam radiation,
ultraviolet radiation, heat or a combination thereof to
form cured coating having a silicone release surface for
releasable contact with a pressure-sensitive adhesive
with substantially all of the silicone contained in the
35 coating composition being anchored to the cured coating
and substantially non-transferable to a pressure-sensitive
adhesive.

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1 12. A product as claimed in claim 11 in which the
reactive silicone is present in an amount of from about
5 to about 15 percent by weight of the coating composition.

5 13. A product as claimed in claim 11 in which the
oligomers are selected from the group consisting of
acrylated epoxies, acrylated polyesters, acrylated poly-
urethanes and mixtures thereof.

10 14. A product as claimed in claim 11 in which the
reactive monomer is a multifunctional monomer.

15 15. A product as claimed in claim 12 in which the
reactive monomer is a multifunctional monomer.

16 16. A product as claimed in claim 15 in which the
reactive silicone is present in an amount of from about
5 to about 15 percent by weight of the coating composition.

20 17. A product as claimed in claim 11 in which the
reactive groups of the silicone are selected from the
group consisting of acrylic groups and mercaptos groups,
oxiranes and mixtures thereof.

25 18. A product as claimed in claim 12 in which the
reactive groups of the silicone are selected from the
group consisting of acrylic groups, mercapto groups,
oxiranes and mixtures thereof.

30 19. A product as claimed in claim 16 in which the
reactive groups of the silicone are selected from the
group consisting of acrylic groups, mercapto groups,
oxiranes and mixtures thereof.

35

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1 20. A curable coating composition comprising from
about 1 to about 30 percent by weight of the coating
composition of a reactive silicone dispersed as a discon-
tinuous phase in 99 to 70 percent by weight of the coating
5 composition of reactive resin phase comprising:

(i) from 50 to 100 percent by weight of the
reactive resin of an oligomer reactive with said reactive
silicone and

10 (ii) from about 50 to 0 percent by weight of
the reactive resin of a reactive monomer, said reactive
silicone being a polydimethyl siloxane having a molecular
weight of at least about 2000 and having pendent therefrom
sufficient reactive groups to react with the reactive
15 group of the oligomer on exposure to the action of electron
beam radiation, ultraviolet radiation or heat to form a
cured coating having a silicone release surface releas-
able from a pressure-sensitive adhesive and in which
substantially all of the silicone contained in the com-
position is anchored to the coating to substantially
20 prevent transfer of the coating to a pressure-sensitive
adhesive.

21. A curable composition as claimed in claim 20
in which the reactive silicone is present in an amount
25 of from about 5 to about 15 percent by weight of the
coating composition.

22. A curable coating as claimed in claim 20 in
which the oligomers are selected from the group consisting
30 of acrylated epoxies, acrylated polyesters, acrylated
polyurethanes and mixtures thereof.

23. A curable coating as claimed in claim 20 in
which the reactive monomer is a multifunctional monomer.

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1 24. A curable coating as claimed in claim 22 in
which the reactive monomer is a multifunctional monomer.

5 25. A curable composition as claimed in claim 24
in which the reactive silicone is present in an amount
of from about 5 to about 15 percent by weight of the
coating composition.

10 26. A curable coating as claimed in claim 20 in
which the reactive groups of the silicone are selected
from the groups consisting of acrylic groups, mercapto
groups, oxirane groups and mixtures thereof.

15 27. A curable coating as claimed in claim 21 in
which the reactive groups of the silicone are selected
from the groups consisting of acrylic groups, mercapto
groups, oxirane groups and mixtures thereof.

20 28. A curable coating as claimed in claim 25 in
which the reactive groups of the silicone are selected
from the groups consisting of acrylic groups, mercapto
groups, oxirane groups and mixtures thereof.

25 29. A curable coating composition comprising:
(a) from about 5 to about 15 percent by weight
of the coating composition of a reactive silicone having
reactive groups selected from acrylic groups, mercapto
groups, oxirane groups and mixtures thereof, dispersed
as discontinuous phase in a from 95 to about 85 percent
30 by weight of the coating composition of a continuous
reactive resin phase comprising:

(i) from about 50 to 100 percent by weight
of the reactive resin of an oligomer reactive with said
reactive silicone and selected from the group consisting

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1 of acrylated epoxy resins, acrylated polyester resins,
acrylated urethane resins and mixtures thereof, and
(ii) from 50 to about 0 percent by weight
of the reactive resin of at least one acrylated multi-
5 functional monomer, said reactive silicone being a poly-
dimethylsiloxane having a molecular weight of at least
about 2,000, said composition having a viscosity of from
about 300 to about 10,000 centipoise and curable on
10 exposure to the action of electron beam radiation, ultra-
violet radiation or heat, or a combination thereof, to
form a cured coating having a silicone release surface
opposed the substrate to which the coating has been
applied for releasable contact with a pressure-sensitive
15 adhesive and in which substantially all of the silicone
contained in the composition is anchored in the coating
and substantially nontransferable to a pressure-sensitive
adhesive.

20 30. A process for producing a release coated sub-
strate which comprises:

(a) applying to a substrate a coating composi-
tion comprising:

25 (i) from about 1 to about 30 percent by
weight of the composition of a reactive silicone
dispersed as a discontinuous phase in from
about 99 to about 70 percent by weight of the
coating composition of a continuous reactive
resin phase comprising:

30 (ii) from about 50 to 100 percent by weight
of reactive resin phase of an oligomer reactive
with said reactive silicone, and

35 (iii) from about 50 to 0 percent by weight
of the reactive resin phase of a reactive
monomer, said reactive silicone being a poly-
dimethylsiloxane having a molecular weight of

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1 at least about 2,000 and having pendent therefrom
sufficient reactive groups to react with the
reactive groups of the oligomer;

5 (b) exposing the coating to the action of
sufficient electron beam radiation, ultraviolet radiation
or heat or a combination thereof to form a cured coating
having a silicone release surface for releasable contact
with a pressure-sensitive adhesive and in which
10 substantially all of the silicone groups are anchored in
the cured coating and substantially non-transferable to
a pressure-sensitive adhesive.

31. A process as claimed in claim 30 in which coating
composition has a viscosity of from about 300 to about
15 10,000 centipoise.

32. A process as claimed in claim 30 in which the
oligomers are selected from the group consisting of
acrylated epoxies, acrylated polyesters, and acrylated
20 polyurethanes and mixtures thereof.

33. A process as claimed in claim 30 in which the
reactive monomer is a multifunctional monomer.

25 34. A process as claimed in claim 32 in which the
reactive monomer is a multifunctional monomer.

35. A process coating as claim in claim 30 in which
the reactive groups of the silicone are selected from
30 the groups consisting of acrylic groups, mercapto groups,
oxirane groups and mixtures thereof.

36. A curable coating as claimed in claim 32 in
which the reactive groups of the silicone are selected

35

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1 from the groups consisting of acrylic groups, mercapto
groups, oxirane groups and mixtures thereof.

5 37. A curable coating as claimed in claim 34 in
which the reactive groups of the silicone are selected
from the group consisting of acrylic groups and mercapto
groups and mixtures thereof.

10 38. A process for forming a release coating substrate
which comprises:

(a) applying to the substrate a coating com-
prising:

15 (i) from about 5 to about 15 percent by
weight of the coating of a reactive silicone
having reactive groups selected from acrylic
groups, mercapto groups, oxirane groups and
mixtures thereof, dispersed as discontinuous
phase in from about 95 to about 85 percent by
weight of the coating of a continuous reactive
20 resin phase comprising:

(ii) from 50 to 100 percent by weight of
the reactive resin of an oligomer reactive
with said reactive silicone and selected from
the group consisting of acrylated epoxy resins,
25 acrylated polyester resins, acrylated urethane
resins and mixtures thereof, and

(iii) from about 50 to 0 percent by weight
of the reactive resin of at least one multi-
functional monomer, said reactive silicone being
30 a polydimethyl-siloxane having a molecular
weight of at least about 2,000, said coating
composition having a viscosity of from about
300 to about 10,000 centipoise;

(b) subjecting the coating to the action of
35 sufficient electron beam radiation, ultraviolet radiation

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1 or heat or a combination thereof to form a cured coating
having a silicone release surface for releasable contact
with a pressure-sensitive adhesive and in which substan-
tially all of silicone is anchored in the cured coating
5 and substantially non-transferable to a pressure-sensitive
adhesive.

10 39. A product comprising substrate having bonded
thereto a cured release coating having a silicone release
surface for releasable contact with a pressure-sensitive
adhesive, said coating formed by coreaction of silicone
present in an amount of from about 1 to about 30 percent
by weight of the coating and a resin contained in a
15 coating composition applied to the substrate, the cure
induced by exposure of the applied coating to the action
of energy supplied by ultraviolet radiation, electron
beam radiation, or a combination thereof induced in a
sufficient amount to anchor the silicone to the coating
whereby the silicone is substantially non-transferable
20 to a pressure-sensitive adhesive.

25 40. A product as claimed in claim 39 in which the
silicone is present in an amount of from about 5 to
about 30 percent by weight of the coating.

41. A product as claimed in claim 39 in which the
silicone is present in an amount of from 5 to about 15
percent by weight of the coating.

30 42. A product comprising a substrate having coating
on at least one side thereof with a cured coating composi-
tion comprised of from about 1 to about 30 percent by
weight of the coating composition of a reactive silicone
dispersed as a discontinuous phase in about 99 to about
35 70 percent by weight of the coating composition or con-

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1 tinuous reactive resin phase comprising from about 50 to
2 100 percent by weight of the oligomer reactive with said
3 reactive silicone and from about 50 to 0 percent by
4 weight of the reactive resin of a reactive monomer, said
5 reactive silicone being a polydimethyl siloxane having a
6 molecular weight of at least about 2000 and having pendent
7 therefrom sufficient reactive groups to react with the
8 reactive groups of the oligomer, said coating being cured
9 on exposure to the action of electron beam radiation,
10 ultraviolet radiation, or a combination thereof to form
11 cured coating having a silicone release surface releasable
12 from a pressure-sensitive adhesive with substantially
13 all of the silicone contained in the coating composition
14 being anchored to the cured coating.

15

43. A product as claimed in claim 42 in which the
reactive silicone is present in an amount of from about
5 to about 30 percent by weight of the coating composition.

20

44. A product as claimed in claim 42 in which the
reactive silicone is present in an amount of from about
5 to about 15 percent by weight of the coating composition.

25

45. A curable coating composition comprising from
about 1 to about 30 percent by weight of the coating
composition of a reactive silicone dispersed as a discontinuous
phase in 99 to 70 percent by weight of the coating
composition of reactive resin phase comprising:

30

(i) from 50 to 100 percent by weight of the
reactive resin of an oligomer reactive with said reactive
silicone and

35

(ii) from about 50 to 0 percent by weight of
the reactive resin of a reactive monomer, said reactive
silicone being a polydimethyl siloxane having a molecular

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1 weight of at least about 2000 and having pendent therefrom
sufficient reactive groups to react with the reactive
group of the oligomer on exposure to the action of electron
beam radiation, ultraviolet radiation or a combination
5 thereof to form a cured coating having a silicone release
surface for releasable contact with a pressure-sensitive
adhesive and in which substantially all of the silicone
contained in the composition is anchored to the coating
to prevent transfer to a pressure-sensitive adhesive.

10

46. A curable composition as claimed in claim 45
in which the reactive silicone is present in an amount
of from about 5 to about 30 percent by weight of the
coating composition.

15

47. A curable composition as claimed in claim 45
in which the reactive silicone is present in an amount
of from about 5 to about 15 percent by weight of the
coating composition.

20

48. A process for producing a release coated sub-
strate which comprises:

(a) applying to a substrate a coating composi-
tion comprising:

25

(i) from about 1 to about 30 percent by
weight of the composition of a reactive silicone
dispersed as a discontinuous phase in from
about 99 to about 70 percent by weight of the
coating composition of a continuous reactive
resin phase comprising:

30

(ii) from about 50 to 100 percent by weight
of reactive resin phase of an oligomer reactive
with said reactive silicone, and

35

(iii) from about 50 to 0 percent by weight
of the reactive resin phase of a reactive

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1 monomer, said reactive silicone being a poly-
dimethylsiloxane having a molecular weight of
at least about 2,000 and having pendent therefrom
sufficient reactive groups to react with the
5 reactive groups of the oligomer;

(b) exposing the coating to the action of
sufficient electron beam radiation, ultraviolet radiation
or a combination thereof to form a cured coating having
a silicone release surface for releasable contact with a
10 pressure-sensitive adhesive and in which substantially
all of the silicone groups are anchored in the cured
coating and substantially non-transferable to a pressure-
sensitive adhesive.

15 49. A process as claimed in claim 48 in which
reactive silicone is present in an amount of from about
5 to about 30 percent by weight of the composition.

20 50. A process as claimed in claim 48 in which
reactive silicone is present in an amount of from about
5 to about 15 percent by weight of the composition.

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1/4

Fig. 1

RT AGING

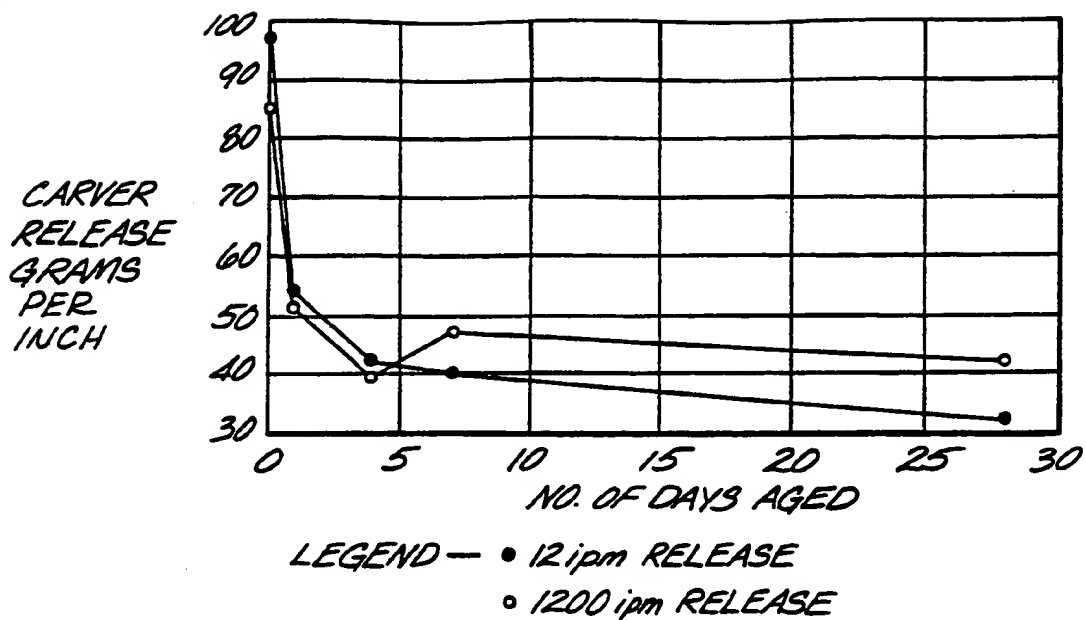
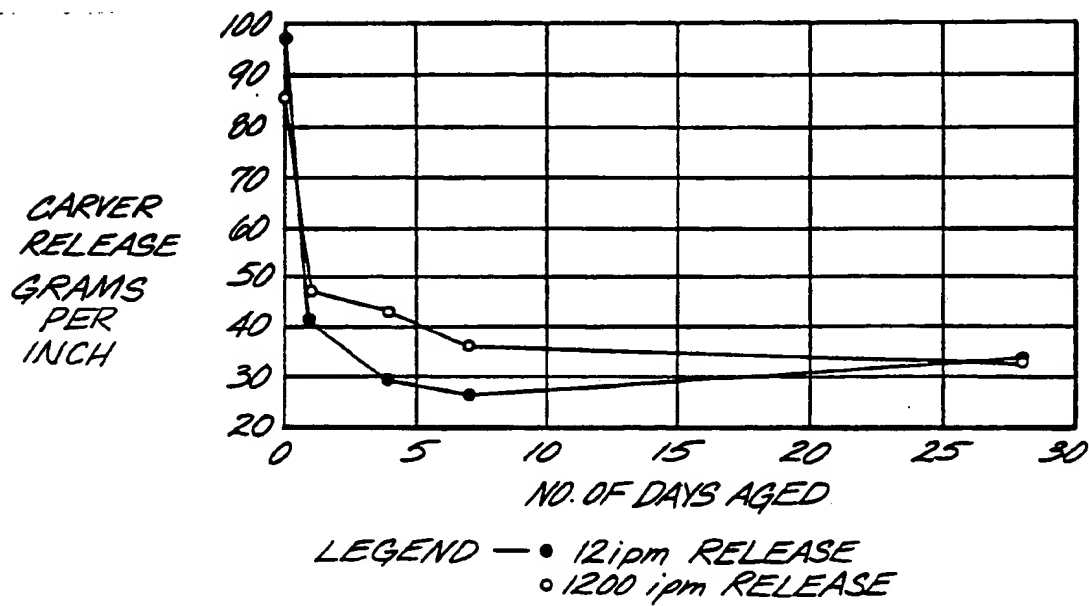


Fig. 2

140°F AGING



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Fig. 3

INITIAL

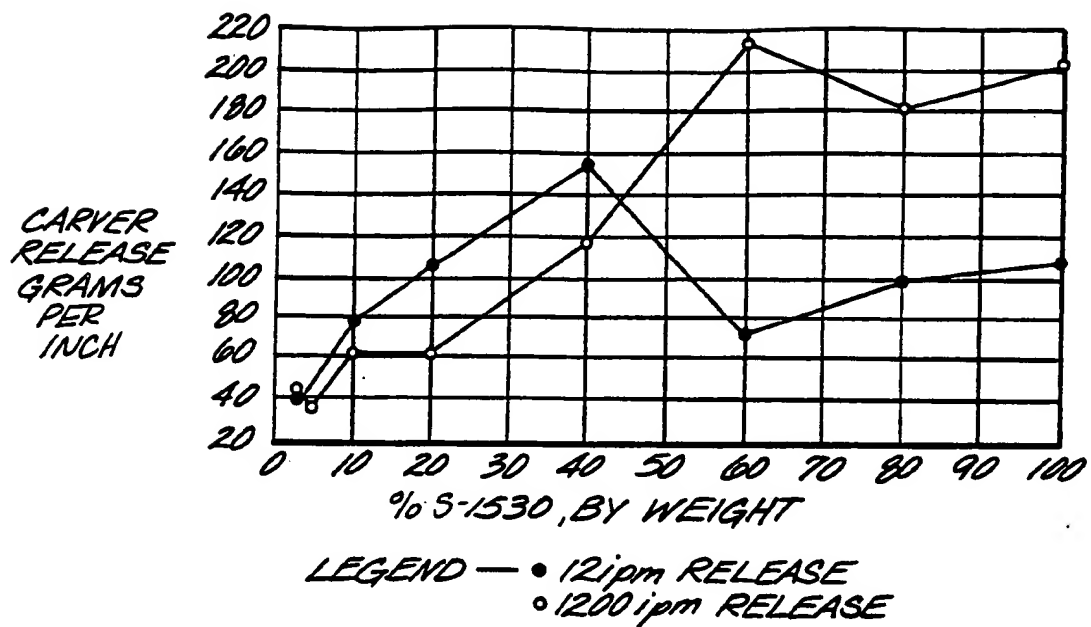
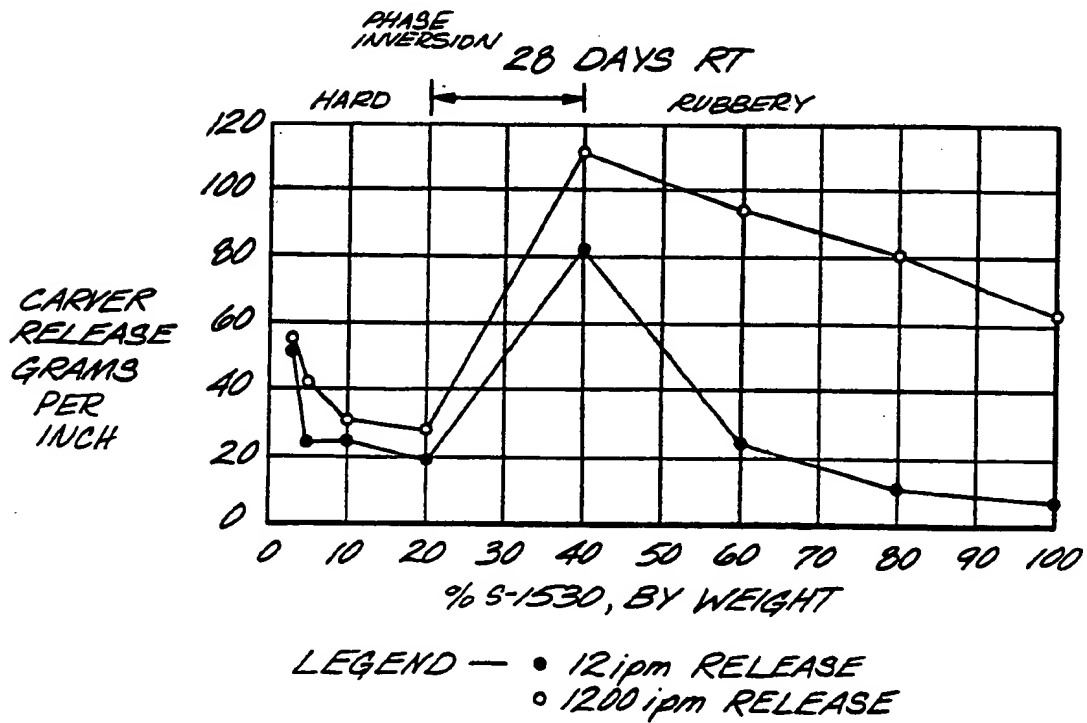


Fig. 4



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Fig. 5

28 DAYS @ 140F

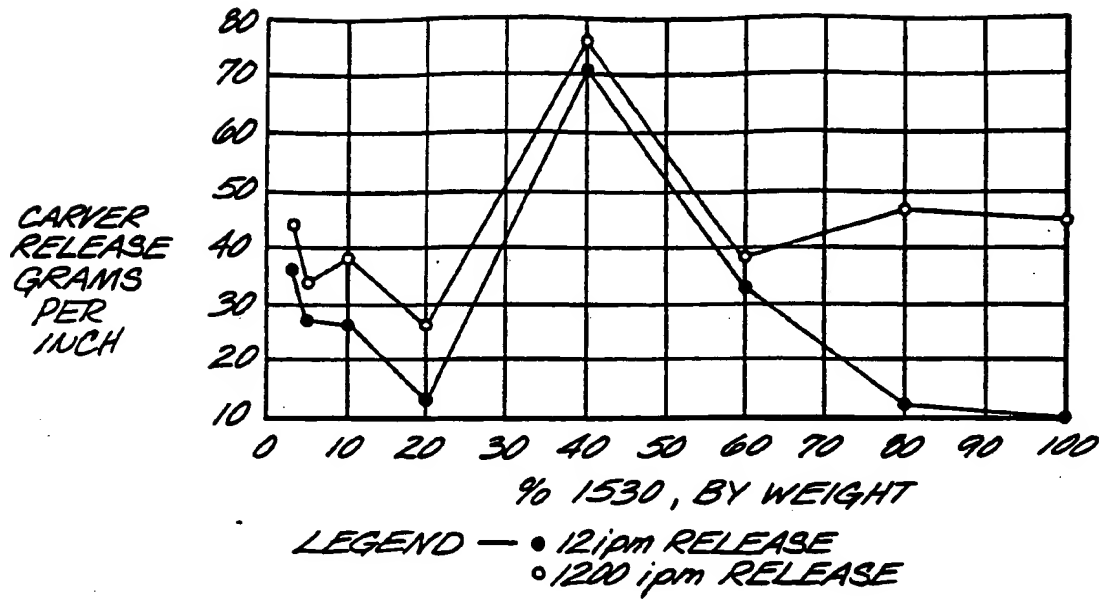
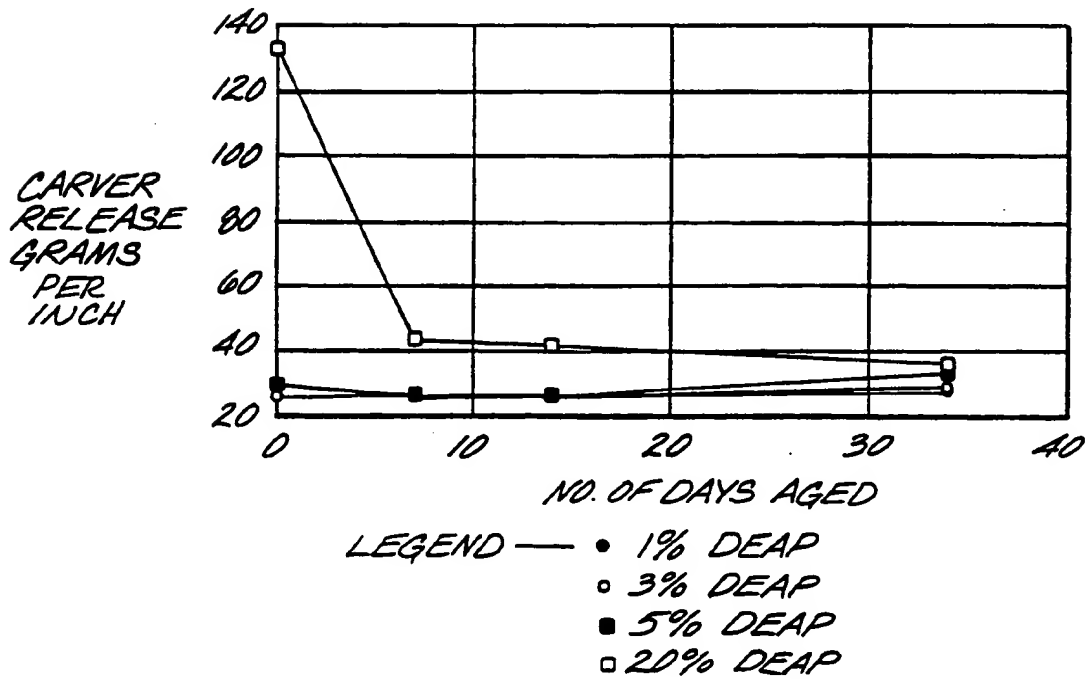
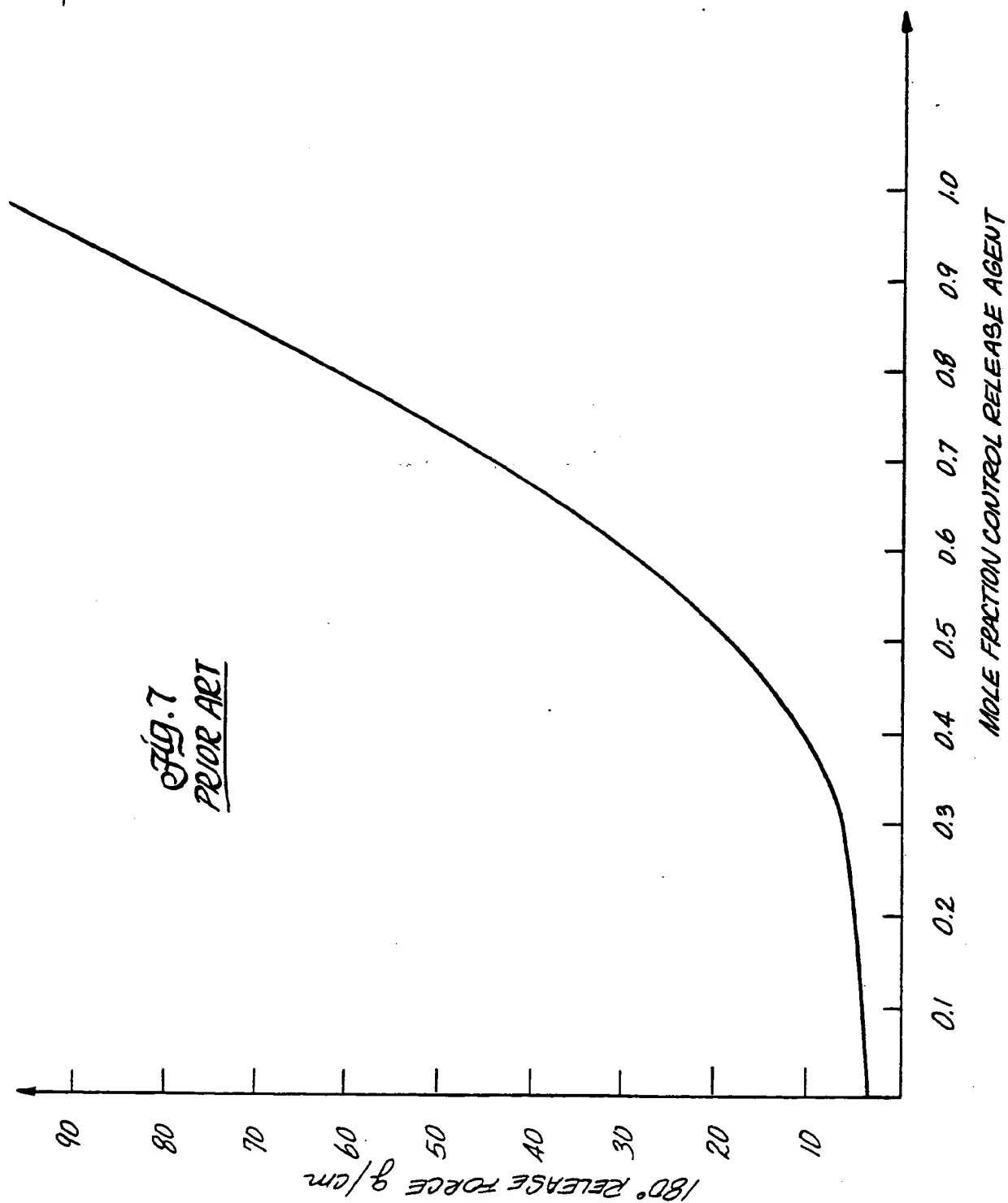


Fig. 6

12 ipm / RT AGED



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INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US88/01160

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC INT. CL. 4: B32B 9/04 US. CL. 428/40, 345, 352, 447; 525/474											
II. FIELDS SEARCHED <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black; margin: 5px 0;">Minimum Documentation Searched ⁷</div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 25%; border-bottom: 1px solid black;">Classification System</th> <th style="width: 75%; border-bottom: 1px solid black;">Classification Symbols</th> </tr> <tr> <td style="vertical-align: top; padding: 5px;">U.S.</td> <td style="vertical-align: top; padding: 5px;"> 428/40, 345, 352, 447 525/100, 474, 476, 479; 528/26 </td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black; margin: 5px 0;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸</div>			Classification System	Classification Symbols	U.S.	428/40, 345, 352, 447 525/100, 474, 476, 479; 528/26					
Classification System	Classification Symbols										
U.S.	428/40, 345, 352, 447 525/100, 474, 476, 479; 528/26										
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹ <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%; border-bottom: 1px solid black;">Category ⁹</th> <th style="width: 60%; border-bottom: 1px solid black;">Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²</th> <th style="width: 30%; border-bottom: 1px solid black;">Relevant to Claim No. ¹³</th> </tr> <tr> <td style="vertical-align: top; padding: 5px;">A</td> <td style="vertical-align: top; padding: 5px;">US, A, 4,288,479 (BRACK) 08 SEPTEMBER 1981</td> <td style="vertical-align: top; padding: 5px;">1-50</td> </tr> <tr> <td style="vertical-align: top; padding: 5px;">A,E</td> <td style="vertical-align: top; padding: 5px;">US, A, 4,668,558 (BARBER) 26 MAY 1987</td> <td style="vertical-align: top; padding: 5px;">1-50</td> </tr> </table>			Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	A	US, A, 4,288,479 (BRACK) 08 SEPTEMBER 1981	1-50	A,E	US, A, 4,668,558 (BARBER) 26 MAY 1987	1-50
Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³									
A	US, A, 4,288,479 (BRACK) 08 SEPTEMBER 1981	1-50									
A,E	US, A, 4,668,558 (BARBER) 26 MAY 1987	1-50									
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>											
IV. CERTIFICATION <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; vertical-align: top; padding: 5px;"> Date of the Actual Completion of the International Search 24 JUNE 1988 International Searching Authority ISA/US </td> <td style="width: 50%; vertical-align: top; padding: 5px;"> Date of Mailing of this International Search Report 02 AUG 1988 Signature of Authorized Officer W. J. VANBALEN </td> </tr> </table>			Date of the Actual Completion of the International Search 24 JUNE 1988 International Searching Authority ISA/US	Date of Mailing of this International Search Report 02 AUG 1988 Signature of Authorized Officer W. J. VANBALEN							
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